50X1-HUM

MAR 1952

CLASSIFICATION CONFIDENTIAL
SECURITY INFORMATION
CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT
CD NO.

COUNTRY	USSR	DATE OF INFORMATION	1953
SUBJECT	Scientific - Chemistry, organophosphorus compounds, toxic compounds		
HOW PUBLISHED	Thrice-monthly periodical	DATE DIST. 16	Sep 1953
WHERE PUBLISHED	Moscow	NO. OF PAGES	4
DATE PUBLISHED	Apr 1953		
LANGUAGE	Russian	SUPPLEMENT TO REPORT NO.	

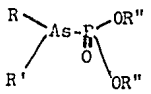
THIS IS UNEVALUATED INFORMATION

SOURCE Doklady Akademii Nauk SSSR, Vol LXXXIX, No 4, pp 693-695.

FIRST SYNTHESIZED REPRESENTATIVES OF CACODYLPHOSPHONIC ACID ESTERS

Gil'm Kamay and E. M-Sh. Bastanov,
Kazan' Chemicotechnological Inst
imeni S. M. Kirova

In 1946, Gil'm Kamay and O. N. Pelorossova (1) synthesized alkyl esters of dialkylcacodylphosphonic, alkylarylcacodylphosphonic, and diarylcacodylphosphonic aids, i. e., compounds having an As-P bond and the general formula:



where R: CH_3-, C_2H_5-, C_3H_5-, n-C_4H_9-; R': C_2H_5-, iso-C_4H_9-, n-C_4H_9-, iso-C_5H_{11}, C_6H_5-; R": C_2H_5-, iso-C_3H_7, n-C_3H_7-, n-C_4H_9-. This was done by arsenating alkyl esters of phosphorous acid and K- or Na derivatives of dialkylphosphorous acids with various secondary halogenoarsines.

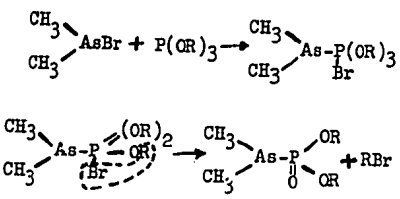
Continuing research in this direction, we undertook the study of the first simple representatives of esters of dialkylcacodylphosphonic acids which we had not yet prepared.

As subjects of our research, we chose dimethylbromoarsine and diethylchloroarsine as the simplest secondary halogenoarsines, which we reacted with methyl, ethyl, n-propyl, iso-propyl, and n-butyl esters of phosphorous acid.

The reaction of dimethylbromoarsine with the middle esters of phosphorous acid was carried out at room temperature and followed by heating on an oil bath for 2 hours to drive off the alkyl halide. The reaction products were then distilled under vacuum. Our experimental data indicate that the middle esters of phosphorous acid react with dimethylbromoarsine according to the following scheme:

CLASSIFICATION CONFIDENTIAL

STATE	X	NAVY	X	NSRB	DISTRIBUTION
ARMY	X	AIR	X	FBI	



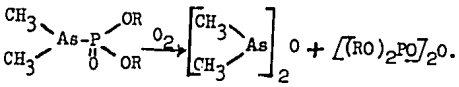
As a result of the experiments carried out on the reaction between dimethylbromoarsine and various alkyl esters of phosphorous acid, we synthesized the esters of dimethylcacodylphosphonic acid listed in Table 1.

The isolated alkyl esters of cacodylphosphonic acid are colorless liquids having an unpleasant and strongly irritating odor. They can be distilled without decomposition only in an atmosphere of an inert gas or in a high vacuum.

Investigations of the chemical properties of the prepared compounds showed that the arsenic-phosphorus bond is easily ruptured as a result of the action of hydrogen halide acids, alkalis, or even oxygen of the air.

Our experiments confirmed that the oxidation of the ethyl ester of dimethylcacodylphosphonic acid with pure oxygen proceeds very energetically and ends with an explosion.

In the case of oxidation by air, the alkyl esters of cacodylphosphonic acid decompose initially according to the scheme:



We succeeded in isolating cacodyl oxide from the reaction products. We did not subject to detailed study the moiety containing phosphorus.

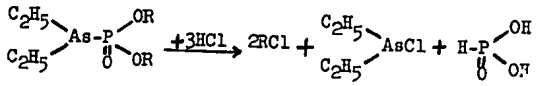
The methyl ester of dimethylcacodylic acid is the most susceptible to oxidation; the ethyl ester of this acid oxidizes more slowly, while the higher homologs are still more inert.

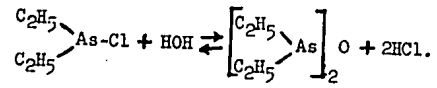
Another series of experiments was carried out to study the reaction of diethylchloroarsine with various alkyl esters of phosphorous acid. Our investigation showed that the reaction between trialkyl phosphite and diethylchloroarsine takes place only upon heating and proceeds with the formation of alkyl chloride and the corresponding diethylcacodylphosphonic ester. Consequently, the mechanism of the reaction is analogous to the above scheme for the reaction between dimethylbromoarsine and trialkyl phosphite. The fundamental physicochemical constants of the diethylcacodyl esters obtained are listed in Table 2.

All of the alkyl esters of diethylcacodylphosphonic acid, whose constitution is seen in Table 2, are colorless liquids with an unpleasant odor.

The yields of the products are low. The chemical properties of these esters are reminiscent of the properties of the esters of dimethylcacodylphosphonic acid. They oxidize gradually in the air to form diethylcacodyl oxide.

Our attempt to prepare free diethylcacodylphosphonic acid by hydrolysis was unsuccessful. The reaction of saponification with 10% hydrochloric acid proceeds with the rupture of the As-P bond and the formation of alkyl chloride and of the oxide of the ethyl analog of cacodyl according to the following scheme:





Detailed study of the stability of the arsenic-phosphorus bond revealed that it is not stable in cacodylphosphonic esters of either group and that it is ruptured as a result of the action of alkalis, halides, and other compounds as well as that of hydrochloric acid or oxygen.

Table 1. Dimethylcacodylphosphonic Acid Esters

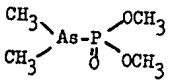
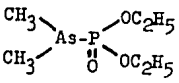
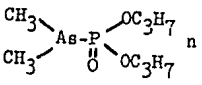
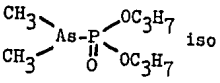
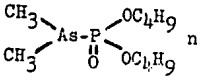
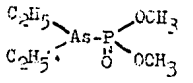
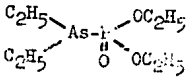
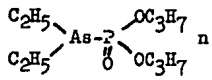
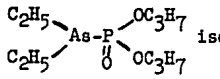
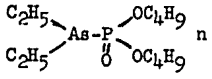
Formula of the Ester	Bp at 1 mm (degrees)	d_0^0	d_0^{10}	Yield (%)
	76.5	1.4011	--	60.5
	83	1.3036	1.2932	74.3
 n	101.5	1.2343	1.2242	64.9
 iso	82-83	1.2112	1.2015	64.4
 n	122-123	1.1933	--	54.1

Table 2. Diethycacodylphosphonic Acid Esters

Formula of the Ester	Bp at 1 mm (degrees)	d_0^0	d_0^{15}	n_D^{15}	Yield (%)
	5- 99.5	1.3205	--	--	29.8
	105.5-106.5	1.2276	1.2129	1.4878	32.2

Formula of the Ester	Bp at 1 mm (degrees)	d_0^0	d_0^{15}	n_D^{15}	Yield (%)
 n	124-125	1.1817	1.1675	1.4901	36.2
 iso	10C-107	1.1678	1.1529	1.4782	30.2
 n	144-145	1.0522	--	--	16.9

BIBLIOGRAPHY

1. Gil'm Kamay, O. N. Belorossova, Izvestiya Acad Nauk SSSR, Otdel Khim Nauk, No 2, 191 (1947); No 2, 198 (1950).

- E N D -